Arabian Journal of Chemistry (2015) **xxx**, xxx–xxx

King Saud University

Arabian Journal of Chemistry

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REVIEW

Application of nanoparticle modified with crown ether in colorimetric determinations

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Received 5 April 2015; accepted 22 July 2015

KEYWORDS

Nanoparticle;
Crown ether;
Colorimetry

Abstract There is a general need to develop simple, rapid, and inexpensive detection assays for diagnostic applications and environmental analysis. Currently, most analyses are performed under laboratory conditions, frequently with the assistance of expensive instruments and trained personnel. Colorimetric sensors as dipsticks or in a chromatographic format would be ideal for the various analyses. These sensors need minimal instrumentation and achieve high sensitivity. In recent years, metallic nanoparticles especially gold nanoparticles and silver nanoparticles have been widely used as colorimetric probes for chemical sensing and biosensing. This interesting application is due to their unique size-dependent, interparticle distance dependent, absorption spectra and solution color. When the nanoparticles approach each other and aggregate, the color of the nanoparticles changes from red to purple (or blue) for gold nanoparticles and from yellow to red (or dark green) for silver nanoparticles respectively. This phenomenon is due to the shift of the surface plasmon band to longer wavelength. Crown ethers are known for the unusual property of forming stable complexes with cations. The oxygen atoms lie in a nearly planar arrangement about the central cation. Today the development of crown ether functional nanoparticle as colorimetric sensors is a subject of considerable interest. In this article we investigated on the use of nanoparticle modified with crown ether for sensing of metal ions and also charged molecules with colorimetric technique.

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Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.arabjc.2015.07.012

Please cite this article in press as: Mohammadzadeh Kakhki, R., Rakhshanipour, M. Application of nanoparticle modified with crown ether in colorimetric determinations. Arabian Journal of Chemistry (2015), http://dx.doi.org/10.1016/j.arabjc.2015.07.012

Contents

1. Introduction

The combination of nanotechnology with chemistry is very important in modern science (Rosi and Mirkin, 2005; Liz Marzn, 2004; Mohammadzadeh Kakhki, 2013, 2015, in press; Rounaghi et al., 2012a). Design of functional nanomaterials is very interesting. It is because of a variety of applications ranging from chemistry to biological sciences. The nanosize metal particles are emerging as an important type of colorimetric reporters because of their extinction coefficients are several orders of magnitude larger than those of organic dyes (Grabar et al., 1995) and the transition of the nanoparticles from dispersion to aggregation leads to a distinct change in color (Link and El-Sayed, 1999; Brust et al., 1995; Mirkin et al., 1996; Demers et al., 2000; Kim et al., 2001; Grabar et al., 1995; Elghanian et al., 1997; Kreibig and Vollmer, 1995; Storhoff et al., 2000). This phenomenon is termed "surface Plasmon absorption" and the color change is due to the coupling of the plasmon absorbances upon aggregation.

Crown ethers (CEs) are known for the unusual property in forming stable complexes with metal cations (Rounaghi and Mohammadzadeh Kakhki, 2009; Rounaghi et al., 2008, 2011a,b, 2012a). Due to this property crown ethers have been applied for various applications such as the construction of sensors (Rounaghi and Mohammadzadeh Kakhki, 2011; Ronaghi et al., 2011; Mohammadzadeh Kakhki and Rounaghi, 2011) and separation systems (Mohammadzadeh Kakhki and Rounaghi, 2011; Rounaghi et al., 2012b). We recently reviewed some of these applications (Mohammadzadeh Kakhki, 2013a,b; Mohammadzadeh Kakhki and Assadi, 2015).

A useful detection system should meet two requirements: a sensing moiety with satisfactory ionic selectivity and a measurable change for the recognition. Crown ethers have often been targeted for connection to molecular scaffolds for the purpose of metal ion sensing materials. For optical transduction methods, crown ethers are usually coupled with a molecular chromophore whose extinction coefficient effects on the detection sensitivity. Most chromophores are nonpolar, and thus, their applications in aqueous media are limited. Recently, nanosized metal particles are emerging as an important type of colorimetric reporters because the extinction coefficient is several orders of magnitude larger than organic dyes and also the transition of the nanoparticles from dispersion to aggregation exhibits a distinct change in color. By taking advantage of the mechanism of color transformation in nanoparticles, in this article we review the ion recognitions by crown ether-attached nanoparticles.

2. Advantages of colorimetric sensors

Colorimetric methods, which have extraordinary sensitivity in the detection of metal ions, environmental monitoring and biological systems (Kim et al., 2001; Zampolli et al., 2007; Choi et al., 2007; Gates et al., 2008), have attracted great attention and they are effective means for such applications; moreover, they can be monitored by the naked eyes. Many of other techniques often are expensive, time consuming, sample retreatment including preconcentration and matrix separation. Therefore, the development of rapid and cost-effective colorimetric sensors for the easy and fast detection of metal and nonmetal ions is very interested.

Significant progress has been made in recent years in the development of functionalized nanomaterials by building blocks for supramolecular structures for sensory applications (Srivastava et al., 2005).

Design of functional nanomaterials is of current interest because of a variety of potential applications ranging from chemistry to biological sciences. Metal and semiconductor nanoparticles exhibit interesting size- and shape-dependent properties. The nanosized metal particles are emerging as an important type of colorimetric reporters because their extinction coefficients are several orders of magnitude larger than those of organic dyes.

Colorimetric sensors based on nanoparticle modified with crown ether are very attractive due to achieve high sensitivity.

2.1. Nanoparticles in colorimetry

By taking advantage of the fact that the transition of nanoparticles from dispersion to aggregation exhibits a distinct change in color, nanoparticles have been used in colorimetric method (Lin et al., 2002). To date, there have been various colorimetric sensors based on the functional metal nanoparticles. Nanoparticles are extremely attractive because of their remarkable optical, electrical and chemical properties, as well as the detection with minimal material consumption. For example, the color of the nanoparticles changes from red to purple (or blue) for Gold nanoparticles (Au NPs) and from yellow to red (or dark green) for Ag NPs respectively. This is due to the shift of the surface plasmon band to longer wavelength (Yin et al., 2002; Garcia et al., 2005). Since nanoparticles have a high surface area to volume ratio, the plasmon frequency is sensitive to the dielectric (refractive index) nature of its interface with the local medium. Any change in the environment of nanoparticles (surface modification, aggregation, medium refractive index, etc.) leads to colorimetric changes of the dispersions and this fact nicely explains the visual sensing ability of these nanoparticles. Au NPs have attracted great interest as a sensor platform because of their easy preparation, biofunctionalization, excellent biostability and distinct spectral properties (Li et al., 2010). The surface plasmon band of gold nanoparticles is located in the visible region of the electromagnetic spectrum and can be effectively controlled by the

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geometry of nanoparticle assemblies (Lu et al., 2010; Ou et al., 2010; Chandirasekar et al., 2011; Hung et al., 2010; Zhang et al., 2012).

2.2. Functionalized nanoparticles

There are two intrinsic drawbacks for the use of unmodified nanoparticles. Firstly, without the help from instruments, identification by the naked eye can at best provide a semi-quantitative result. The results are still hard for unmodified nanoparticles to do a quantitative analysis. Secondly, the non-modified nanoparticles to some extent have problem of interferences than ligand-stabilized nanoparticles. In particular, the design and synthesis of AuNPs functionalized with targeted functional molecules, owning to their unique optical properties have been attracted much attention. Therefore these nanoparticles have been extensively used as modern ultrasensitive detection and imaging probes for reorganizing events (Stewart et al., 2008; Ghadiali and Stevens, 2008; Daniel and Astruc, 2004).

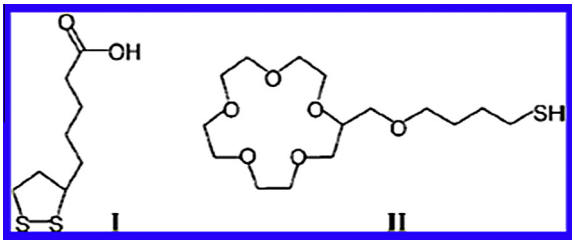
The design of functional nanomaterials is of current interest because of a variety of potential applications ranging from chemistry to biological sciences. Metal and semiconductor nanoparticles exhibit interesting size and shape-dependent properties (Burda et al., 2005). Because of this unique optical property, functionalized nanoparticles have been extensively explored as probes for sensing/imaging in a wide range of analytes/targets, such as alkali metal ions (Obare et al., 2002), heavy metal ions (Liu and Lu, 2004; Chansuvarn and Imyim, 2012; Qi et al., 2012; Xu et al., 2012) or molecules (Otsuka et al., 2001).

Crown ether derivatives, due to their unique coordination chemistry exhibited inherent sensor selectivity toward various metal ions. In recent years, nanometer-sized supramolecular assemblies created by the simple inclusion complexation of crown ethers and guest molecules have attracted more and more attention because of their potential to serve as functional materials.

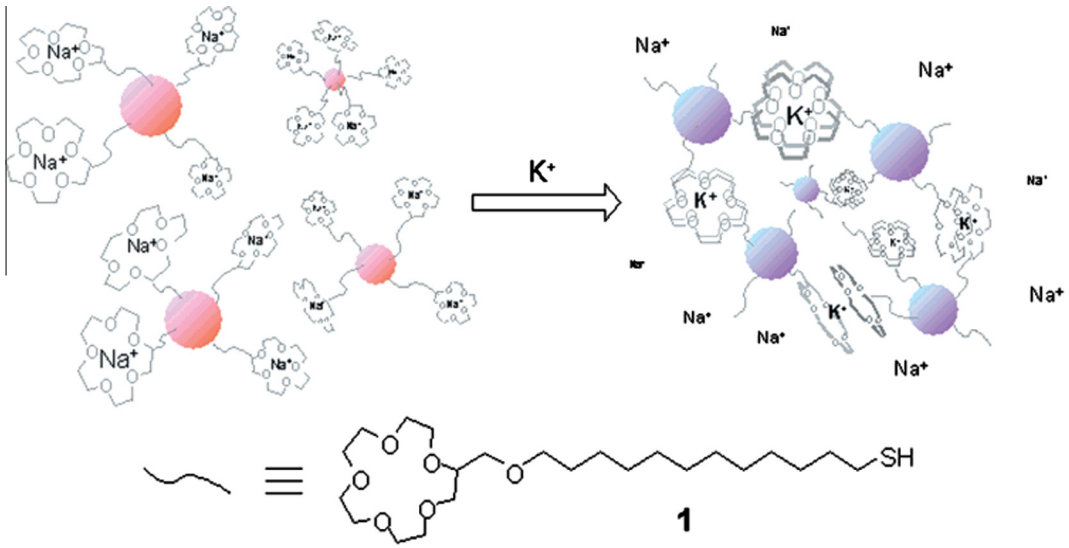
3. Application of nanoparticle modified with crown ether in colorimetry

By taking advantage of the fact that the transition of nanoparticles from dispersion to aggregation exhibits a distinct change in color, therefore the application of functionalized nanoparticles is very interested in recent years. In particular Gold nanoparticle based colorimetric assay is very attractive, since it does not utilize light sensitive dye molecules, lengthy protocols or sophisticated instrumentation. Thereby their employment as sensor, helps to overcoming some of the limitations of more conventional methods.

In recent years, much effort has been devoted to the design of metallic nanoparticles-based sensors for the detection of heavy metal ions in environmental samples. Au NPs are emerged as promising probes in colorimetric assays, because of their high extinction coefficients (10^8–10^{10} M^{-1} cm^{-1}) in the visible region and distinct color change that attributes between their mono-dispersion and induced-aggregation states, which can be observed with bare eye. The ultra-trace target metal ions were selectively identified by integrating functionalized Au NPs as colorimetric sensors in UV–visible spectrometry. In a work (Lin et al., 2011) a strategy for Pb^{2+} ion recognition by aza crown ether-attached nanoparticles has



Scheme 2 (I) Thioctic acid (TA) and (II) 2-(4-mercaptobutyloxy)methyl-15-crown-5 ether (15-crown-5-$CH_2O(CH_2)_4SH$ or 15C5-C4-SH (Wu et al., 2008).



Scheme 1 Schematic representation of the K^+-induced aggregation via sandwich complexation of crown-thiol molecule 1 in a sodium-containing solution (Lin et al., 2002).

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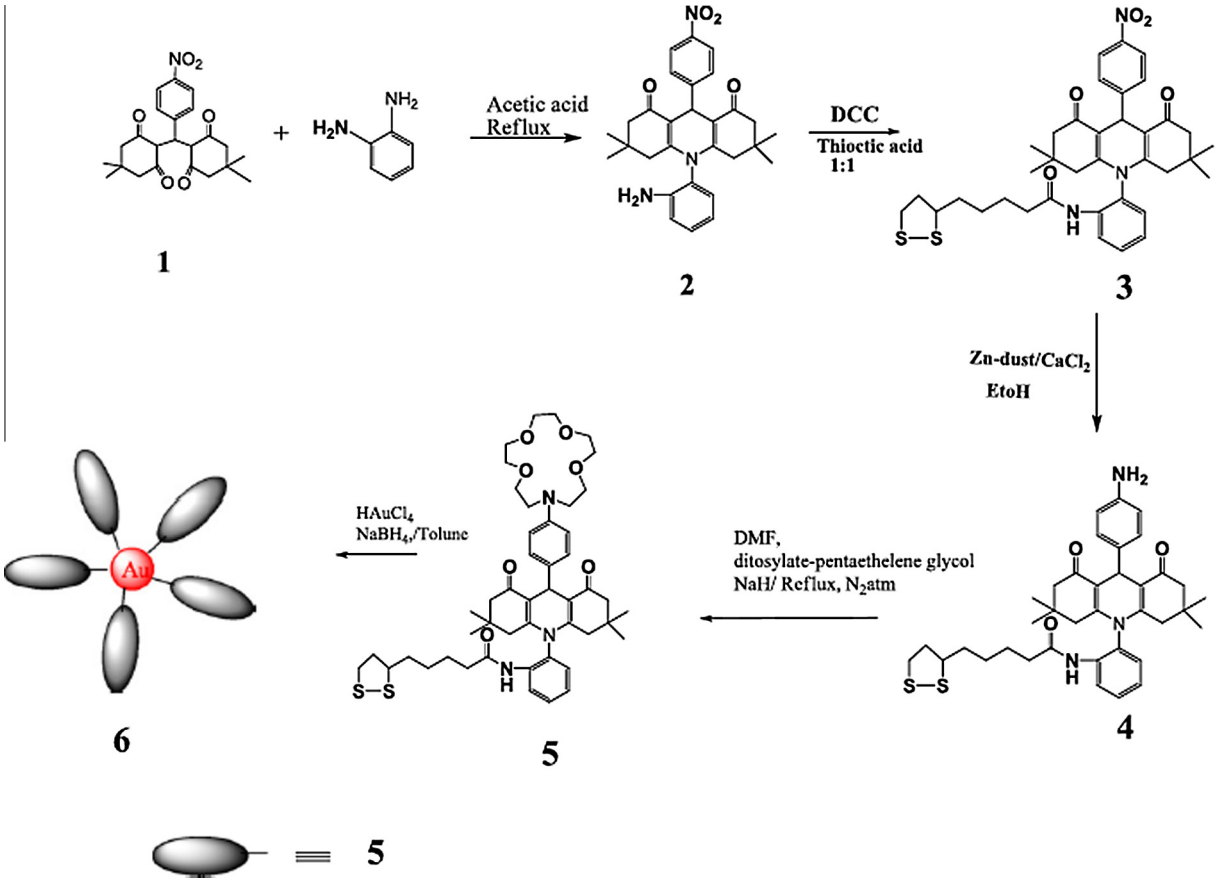
been reported. In this work recognition of Pb^{2+} ion is carried out via simple host–guest interactions that induced an easy-to-read color change. This work represents an initial study of potentially novel sensing nanomaterials that utilize the ionophoric capacity of aza crown ethers. Interestingly, this crown ether–AuNP system can selectively recognize Pb^{2+} even by the naked eye. Also they are small enough to be considered for *in vivo* and remote sensing applications as well as portable measurement devices.

In the other Report (Lin et al., 2002) an efficient recognition of K^+ by 15-crown-5 functionalized gold nanoparticles in aqueous matrix containing physiologically important cations, was carried out. Upon exposure to K^+, the colloidal solution changes from red to blue, in response to surface plasmon absorption of dispersed and aggregated nanoparticles. The concentration ranges of K^+ detected in this study are 0.099–0.48 mM and 7.6–0.14 mM, when concentrations of colloidal gold are 54.9 and 7.1 nM, respectively. Recognition of K^+ and formation of the aggregates are proposed via a sandwich complex of 2:1 between 15-crown-5 moiety and K^+.

As sketched in Scheme 1, the gold nanoparticle was functionalized with the 15-crown-5 and proposed a novel scheme of K^+ recognition by nanoparticle-networking through the sandwich complexes. In summary, the results show that gold nanoparticles modified with 15-crown-5 in water exhibit excellent selectivity toward K^+, resulting in the change in solution color. TEM and UV–visible measurements showed that K^+ recognitions are carried out by aggregation networked by the sandwich complexation. Also this dispersion-aggregation transition can be used as a general detection scheme for spectroscopically inactive species.

By taking advantage of the high extinction coefficients of AuNPs, successful demonstration for the pretreatment of the complicated urine samples was reported (Wu et al., 2008). To improve the analytical performance, most efforts in this research field focus on the design and synthesis of the sensing elements to increase the density of AuNPs. In this way satisfactory LODs could also be obtained by minimizing the electrostatic repulsion between AuNPs. Therefore this system begins with thioctic acid-stabilized AuNPs which are subsequently modified with 15-crown-5 ether for the recognition of K^+ cation. The coverage of crown ether on AuNPs was adjusted by place-exchange reactions and reached a limiting value which was dependent on the ratio of the number of the incoming crown ether to that of thioctic acid already on AuNPs. In this work with 4-day modification, the coverage of crown ether to the total thiol legs was found in the range of 47–92%. An exhaustive examination of eight types of 15C5-C4-/TA-AuNPs revealed that the sensitivity and LODs were a function of the coverage of crown ether moiety and that the one with an 87% exchange ratio (namely, 21.4× AuNPs) exhibited the best analytical performance. The potassium sensor is denoted 15C5-C4-/TA-AuNPs that the AuNPs are biofunctionalized by thioctic acid (TA, and 2-(4-mercaptobutyloxy)



Scheme 3 Schematic illustration of synthesis and assembly of ACEADD-GNPs via the reaction of $HAuCl_4$ with ACEADD (Velu and Ramakrishnan, 2010).

methyl-15-crown-5 ether (15-crown-5-$CH_2O(CH_2)_4SH$ or 15C5-C4-SH Scheme 2.

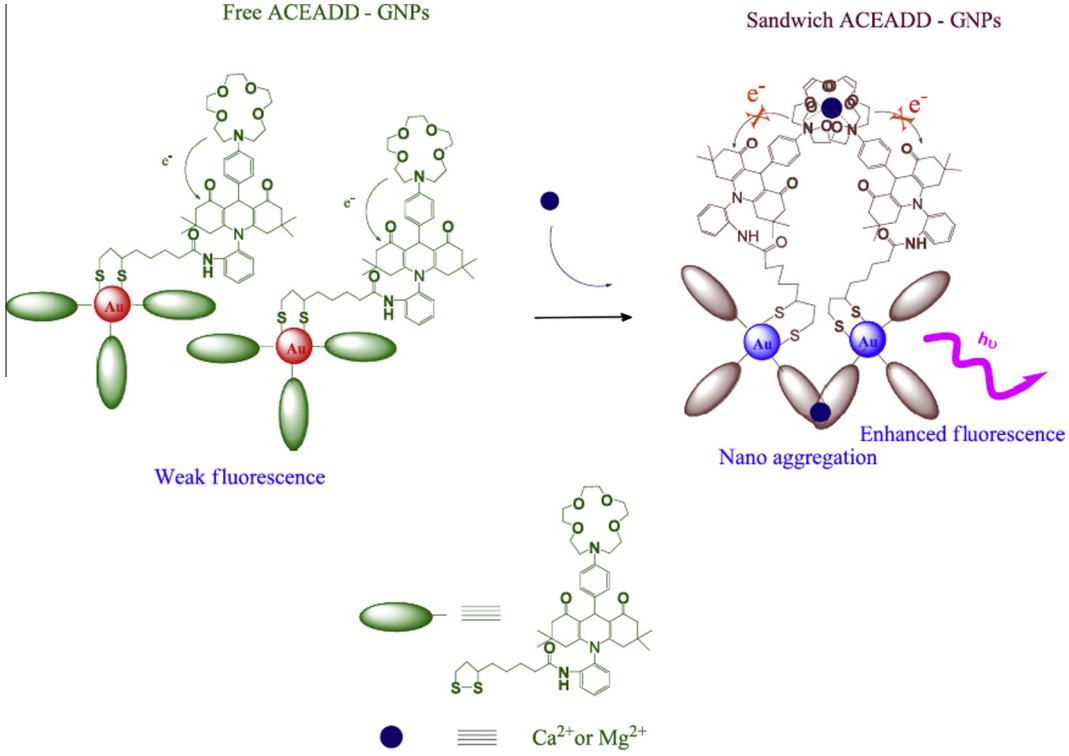
In the other work, aza-crown ether acridinedione-functionalized gold nanoparticles (ACEADD-GNPs) chemosensor, was developed (Velu and Ramakrishnan, 2010). Fluorescence titration with different cation salts in an acetonitrile solution of ACEADD showed an increase in the fluorescence intensity due to PET suppression, and the color change is attributed to the aggregation of nanoparticles. The synthetic procedure is shown in Scheme 3.

A highly specific binding for both Ca^{2+} and Mg^{2+} ions, is achieved by the cation-induced sandwich-like structure of the aza-crown ether acridinedione-AuNPs (Scheme 4). The significant change in color demonstrates that the ACEADD-GNPs recognize Ca^{2+} and Mg^{2+}. The ACEADD-capped gold nanoparticle's colloidal solution appears red. Upon the addition of Ca^{2+} and Mg^{2+} the solution immediately turns blue. This phenomenon is due to shifting of surface plasmon resonance peak as reported by Patel et al. (2009) and Lin et al. (2002).

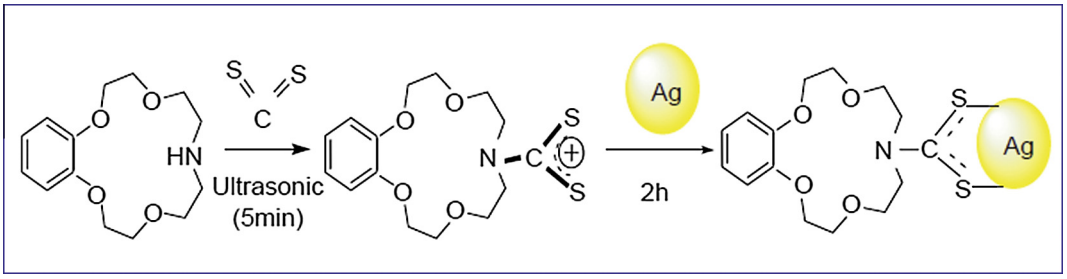
Also a colorimetric method to identify Ba^{2+} ions in solution by ACE-Ag NPs was developed (Li et al., 2010). The method of ACE-Ag NPs preparation is shown in Scheme 5. In the presence of Ba^{2+} ions, the specific binding of AgNPs provides an accurate real-time measurement and quantification in the UV spectrophotometer. This method was simple and low cost and could be directly observable with high sensitivity without the need of sample preconcentration or pretreatment.

On the basis of the ability of crown ether to interact with Ba^{2+} according to a sandwich-like mode (Liu and Lu, 2004), ACE in the surface of Ag NPs can form a sandwich structure with Ba^{2+} cations as shown in Scheme 6(C).

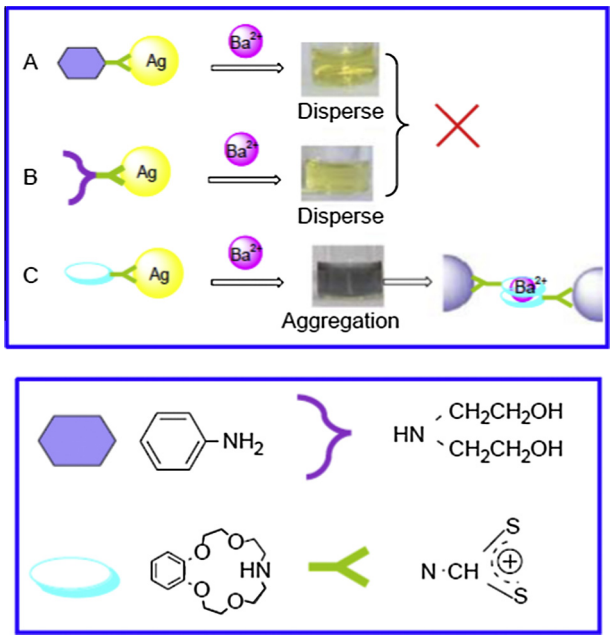
In order to study the recognition mechanism of ACE-AgNPs for Ba^{2+}, diethanolamine (DEA) and aniline modified AgNPs were used for experiment control. In contrast to ACE-



Scheme 4 The possible mechanism of the phenomenon of binding of the free ACEADD-AuNPs with Ca^{2+} and Mg^{2+} (Velu and Ramakrishnan, 2010).



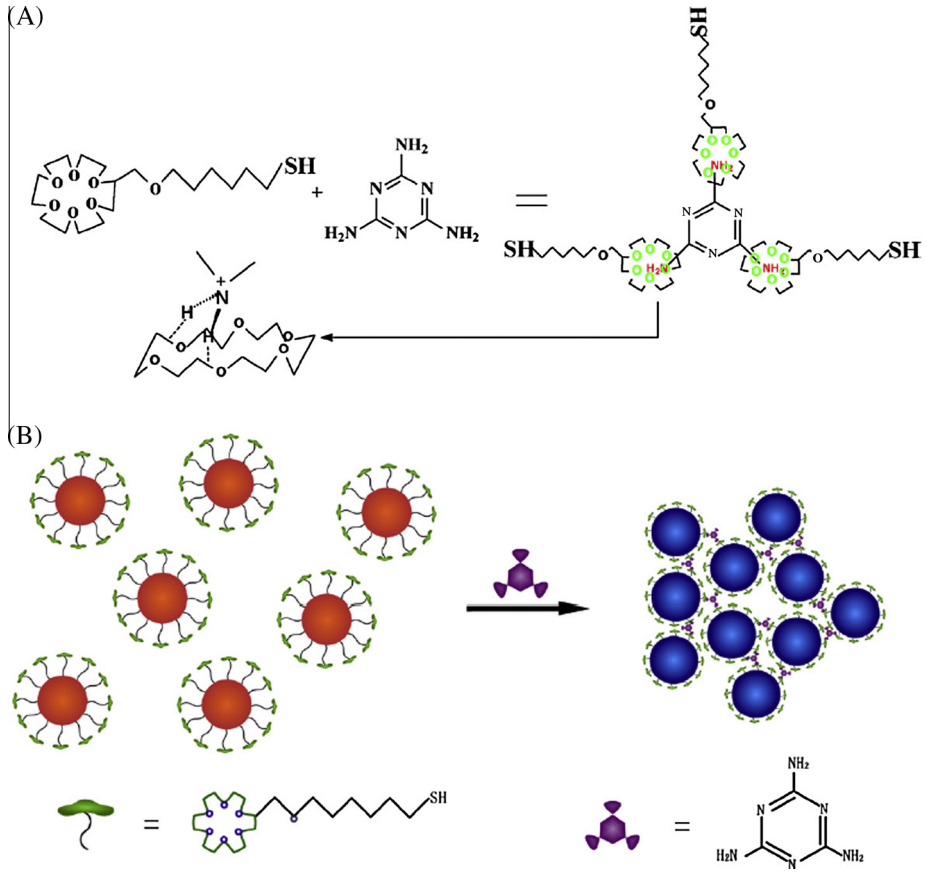
Scheme 5 Synthesis of ACE-Ag NPs (Li et al., 2010).



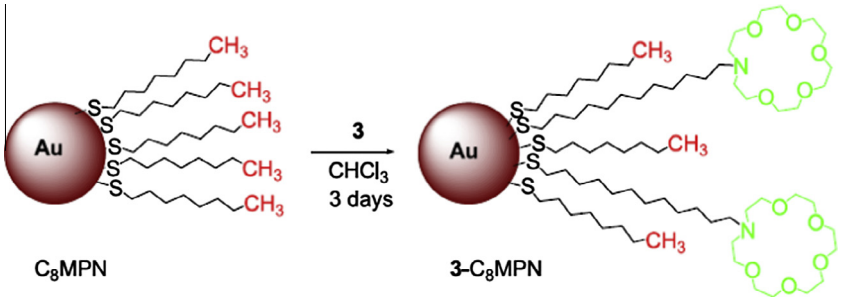
Scheme 6 Schematic illustration of the aggregation of the ACE-Ag NPs in the presence of metal ions (Ba^{2+}) Liu and Lu, 2004.

Ag NPs, aniline-modified Ag NPs were designed to explore whether the benzene ring affects the selectivity, while DEA-Ag NPs were designed with the similarity structure without the ether ring in order to further explore the ability of ACE. Aniline and DEA do not have a similar cyclic structure for the unique response to Ba^{2+} (see Scheme 6(A and B)). According to hard and soft acid and base theory, nitrogen that comes from ACE provides a good coordination site for the barium ion (James and Shinkai, 1995). It is reasonable to believe that ACE-Ag NPs can have a good recognition of Ba^{2+} through the sandwich structure. The ACE-Ag NPs can also have a good recognition of Ba^{2+} without interference with other metal ions.

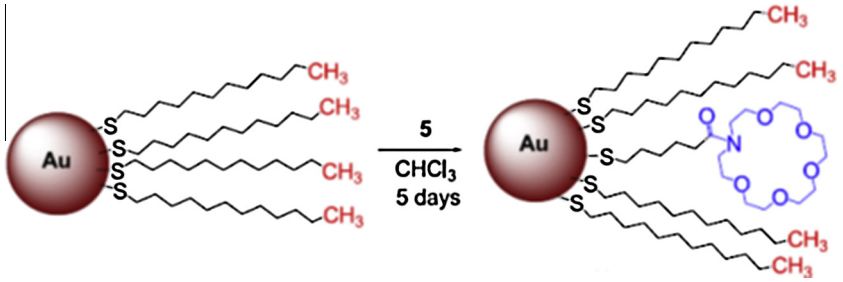
Developing an easy, fast and sensitive method for the routine melamine detection is of great importance. In a report (Kuang et al., 2011), the colorimetric sensing of melamine, based on the 18-crown-6 ether functionalized gold nanoparticles (AuNPs) through the formation of cavity complexes with amines was investigated (Scheme 7). Based on high extinction coefficients and spectral sensitivity of the surface plasmon resonance band of the AuNPs, the rapid and sensitive melamine detection was achieved both visually and spectroscopically. Under the optimal conditions, melamine could be selectively detected in a concentration range from 10 to 500 ppb with a limit of detection as 6 ppb, which is much lower than the strictest melamine safety requirement of 1 ppm. This method



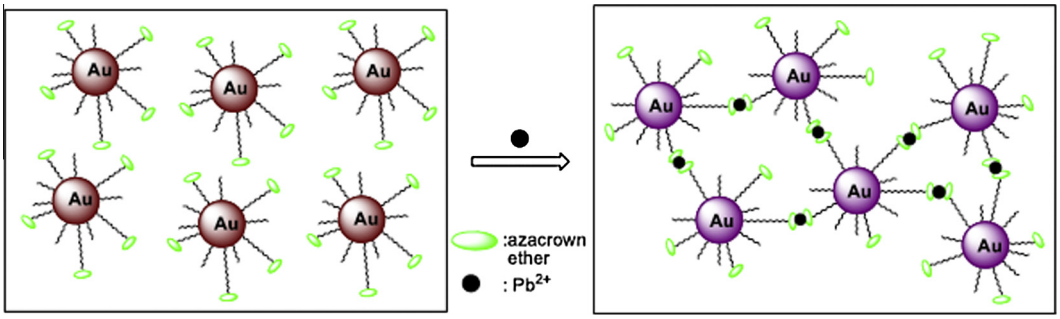
Scheme 7 Schematics of the melamine sensing with 18-crown-6-thiol-modified AuNPs. (A) Specific interaction in the complex between the crown ether and melamine; (B) melamine-induced aggregation of 18-crown-6-thiol-modified GNPs (Kuang et al., 2011).



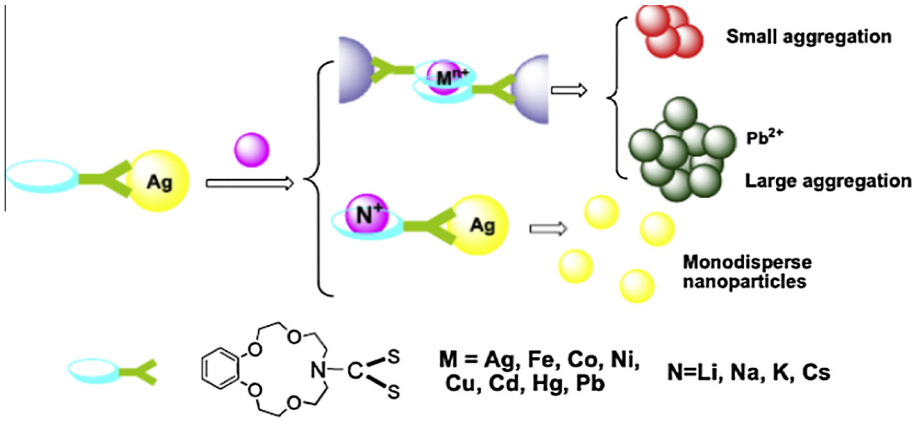
Scheme 8 Synthesis of gold nanoparticles modified with monoazacrown ether-ended thiol 3 bearing ionophore moiety freely available at the surface through place exchange reaction (Alizadeh et al., 2010).



Scheme 9 Synthesis of gold nanoparticles modified with monoazacrown ether-ended thiol 5 through place exchange reaction (Alizadeh et al., 2010).



Scheme 10 Schematic representation of the Pb^{2+}-induced aggregation via sandwich complexation of azacrown ether-capped gold nanoparticles in a lead-containing solution (Alizadeh et al., 2010).



Scheme 11 The possible mechanism of metal-ion-induced aggregation of ACE-Ag NPs (Zhang et al., 2011).

showed good selectivity and practicality for melamine detection. Crown ether assembly of AuNP also opens a route for the formation of three-dimensional pseudorotaxane-like assemblies of nanoparticles that can be applicable to a variety of amine-bearing ligands.

The 18-crown-6 ether can form a 1:1 pseudorotaxane-like structure with melamine and can be easily conjugated to AuNPs via –SH group. After the host–guest recognition, a complex is formed through the interaction of the ether oxygen atoms and diimide moieties between the 18-crown-6 and melamine via complementary NH···O and NH···O hydrogen bonds. This new protocol achieved the detection of melamine through the formation of cavity complexes taking advantage of the presence of several amine groups in the molecule with an excellent LOD as low as 6 ppb, a wide linear range from 10 to 500 ppb, and acceptable reproducibility and specificity.

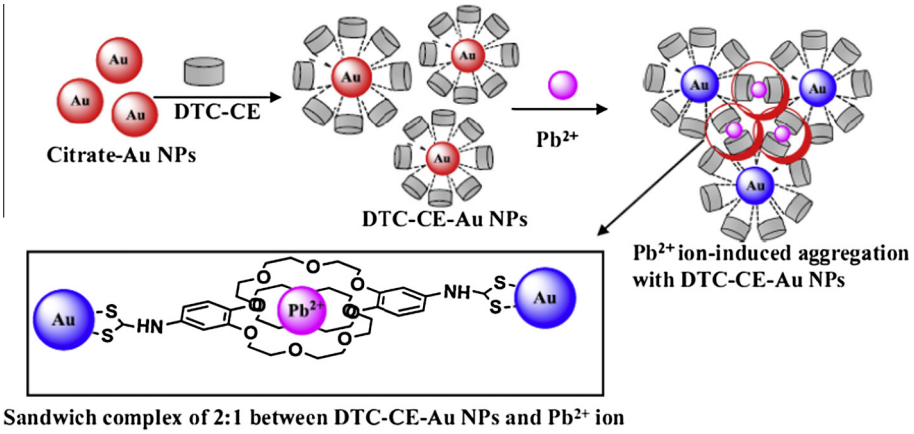
In an interesting work (Alizadeh et al., 2010) a gold nanoparticle (AuNPs)-based colorimetric sensor for selective detecting of Pb(II) in aqueous solution has been developed. Monodisperse AuNPs (approx. 2.0 nm diameter) have been prepared facilely and further modified with an alkane thiol-bearing monoazacrown ether terminus. These AuNPs are shown to selectively sense Pb^{2+} through color change, which is visually discernible by an appearance of the surface plasmon band at 520 nm. The recognition mechanism is attributed to the unique structure of the monoazacrown ether attached to AuNPs and metal sandwich coordination between two aza crown ether moieties that are attached to separate nanoparticles. This inter-particle cross-linking results in an aggregation and apparent color change from brown to purple. Additionally, TEM experiments support the optical absorption data proving the aggregation between aza crown ether-capped gold nanoparticles. This AuNP-based colorimetric assay is a facile and robust method and allows fast detection of Pb^{2+} at ambient temperatures. More importantly, the developed technique does not utilize enzymatic reactions, light-sensitive dye molecules, lengthy protocols or sophisticated instrumentation.

Schemes 8 and 9 demonstrated the modification of Au nanoparticle with monoaza crown ethers. However, only the functionalized monolayers perform actively and the others silently take the passive role.

It is believed that the lack of color change for 5-C12MPN solution, even after adding 1.5 mM Pb^{2+} ions, relies on the geometry of mixed monolayers (matrix) immobilized on gold nanoparticles. As depicted in Scheme 9, the terminal azacrown moieties are completely embedded within the longer co-adsorbed monolayers (dodecane thiols) and hence they are not freely available to the metal ion to form complexes and lead to aggregation and color change. In contrast, in the case of 3-C8MPN, the chain length of the aza crown ether ended layers is fairly longer than that of co-adsorbed methyl-ended layers (Scheme 8). This arrangement of the monolayers on 3-C8MPN demonstrates a system bearing the ionophores (aza-crown moieties) freely available to analyte (Pb^{2+}) at the surface of nanoparticles which allows analyte-trigger disaggregation of 3-C8MPN. These results clearly confirm that the matrix can play an active role in shaping the geometry and conformation of the sensing moiety and in the diminution or improving the recognition performance.

In this work, upon adding Pb^{2+}, the modified AuNPs solution changes from brown to purple which is easy to detect by the naked eye. The recognition of Pb^{2+} triggers particle aggregation is via simple metal coordination between two azacrown ethers that are attached to separate nanoparticles. UV–visible measurements and TEM analysis suggest that the event of Pb^{2+} recognition is signaled by aggregation networked by the sandwich complexation (Scheme 10). The aggregation of the azacrown-capped nanoparticles via selective complexation with Pb^{2+} is remarkably efficient and this ionophore-modified AuNP-based sensor is appreciated for application in the detection of total soluble Pb(II) in aqueous solutions. This system is a rapid, cost-effective and enzyme free colorimetric sensor for easy and fast detection of Pb^{2+} ions by the naked eye without resorting to any expensive instruments.

In the other work a highly selective and ultrasensitive dynamic light scattering (DLS) assay for lead detection using aza-crown-ether-modified silver nanoparticles (ACE-Ag NPs) has been demonstrated (Zhang et al., 2011). It is interesting to fabricate aza-crown-ether (ACE)-modified Ag NPs as sensors for transition metal ions, because ACE can bind well with metal ions (Muegge and Richter, 2002; Li et al., 2007; Williams et al., 2003). A simple and efficient nanoconjugate technology named dithiocarbamate (Morf et al., 2010; Park et al., 2010;

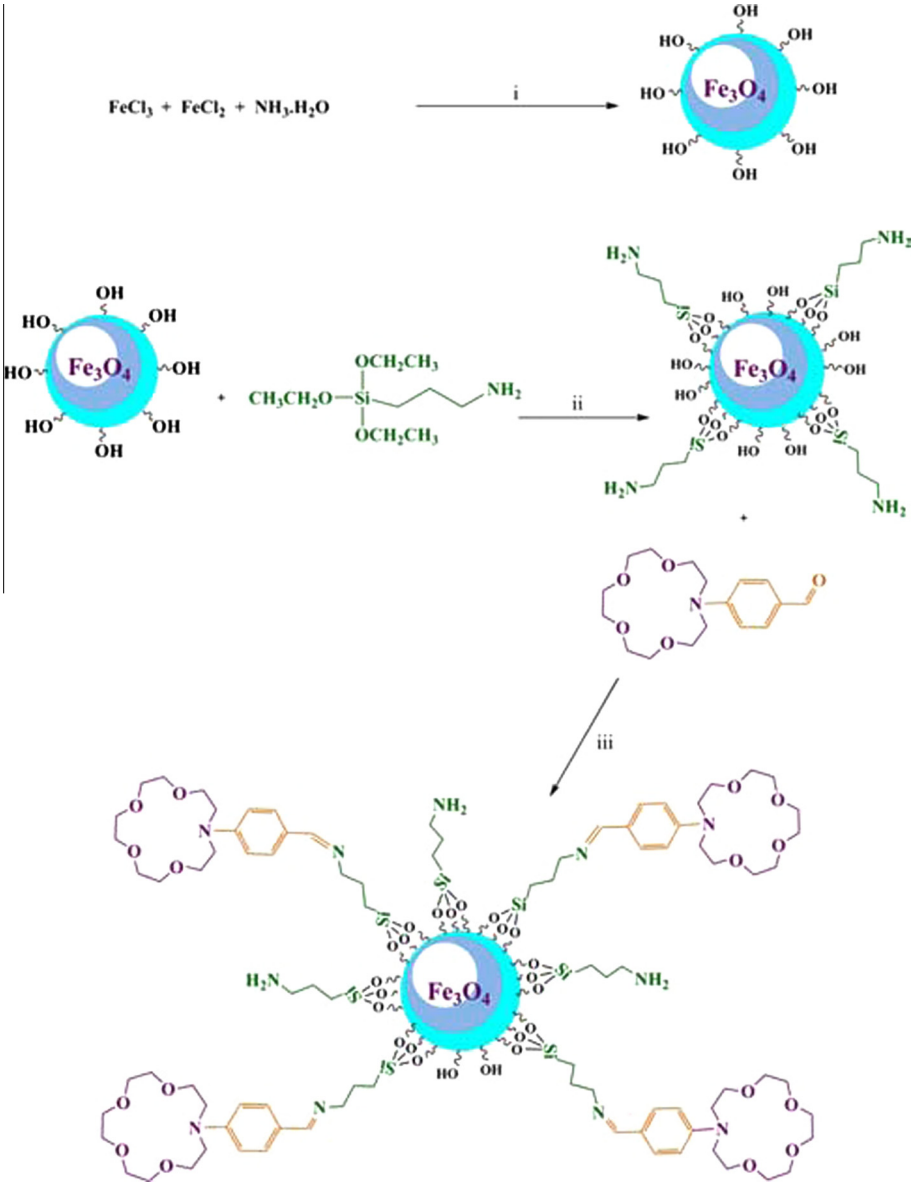


Scheme 12 Schematic representation of Pb^{2+} ion induced DTC-CE-Au NPs aggregation via sandwich complex formation (Mehta et al., 2014).

Zhao et al., 2005; Tong et al., 2006; Vickers et al., 2006) (DTC) was adapted to synthesize azacrown-ether-modified silver nanoparticles (ACE-Ag NPs) for Pb^{2+} detection. ACE-Ag NPs cannot have a good selectivity toward metal ions. In order to solve the problem, a more sensitive DLS method was applied. It is known that DLS is a powerful method for the determination of small changes in particle sizes (Tian et al., 2010), and it can be used as an efficient method for the detection of size changes of metal nanoparticles. From the analysis of data, it is reasonable to believe that Pb^{2+} induces the aggregation of ACE-AgNPs. The possible mechanism is shown in Scheme 11. This study shows that Pb^{2+}-induced nanoparticle aggregation was the most obvious which can be easily monitored by the more sensitive DLS assay.

In this work the detection limit was 0.25 pM (1.03 ppt) in water. Therefore Pb^{2+} DLS assay approach is more simple, convenient and sensitive than colorimetric and UV–Vis spectra detection, which demonstrates a good prospect in actual sample detection.

In the other work, a crown ether based selective colorimetric sensing scheme for the determination of Pb(II) ion by using gold nanoparticles modified with dithiocarbamate derivative of 4′-aminobenzo-18-crown-6 was developed (Mehta et al., 2014). The effective Pb^{2+} ion-induced DTC-CE-Au NPs aggregation was achieved by the sandwich complex formation between multiple DTC of 4′-aminobenzo-18-crown-6-capped Au NPs and Pb^{2+} ion (2:1) (Scheme 12), yielding a red-shift in SPR peak of DTC-CE-Au NPs. The Au NPs aggregation was achieved by the matching of 4′-aminobenzo-18-crown-6-cavity size with the ionic radius of Pb^{2+} ion. As a result, this method showed good linearity in the range of 0.1–75 μM with a detection limit of 50 nM. The DTC-CE-Au NPs probe provides a simple analytical tool for the determination of Pb^{2+} ion with good selectivity and sensitivity. Therefore, this



Scheme 13 Synthetic route for the preparation of (Fe_3O_4-APTES Crown). (i) NH_3·OH, stirred under N_2, 80 °C, 2 h; (ii) stirred under N_2, 40 °C, 2 h; (iii) reflux under N_2, dry toluene, 2 days (Bayrakcl et al., 2013).

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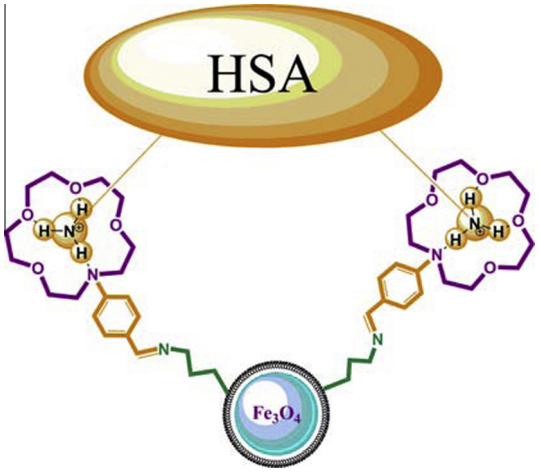
ionic-radius based DTC-CE-Au NPs sensor can be suitable for selective sensing of Pb^{2+} ion complex samples with minimized sample preparations.

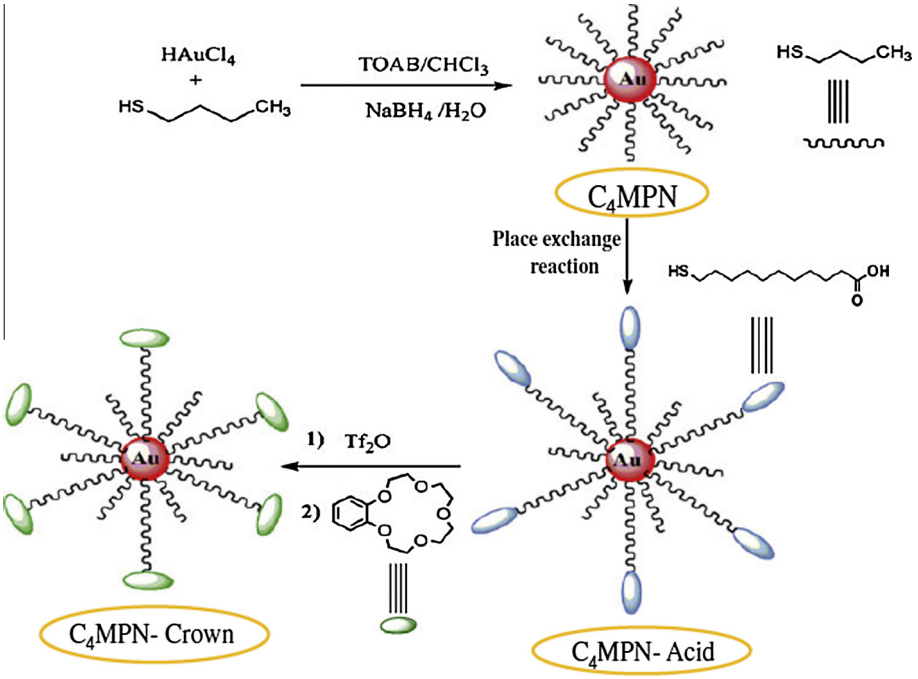
In a report the human serum albumin (HSA) binding studies were carried out by using magnetite nanoparticle containing azacrown ether moieties *via* solid–liquid extraction process (Bayrakcl et al., 2013). The structure of the newly prepared magnetite nanoparticle was clarified by using attenuated total reflectance (ATR) infrared spectroscopy, scanning electron microscopy (SEM), UV–Vis and elemental analysis. Analytic results indicated that modification of the surface of the magnetite nanoparticles with azacrown ether derivative was successfully carried out. The protein binding studies exhibited that the modified magnetite nanoparticles could be efficiently used for the binding of the human serum albumin (HSA) in aqueous solutions *via* non-covalent interaction between crown ether cavity and amino group of the protein. The synthetic route is shown in Scheme 13.



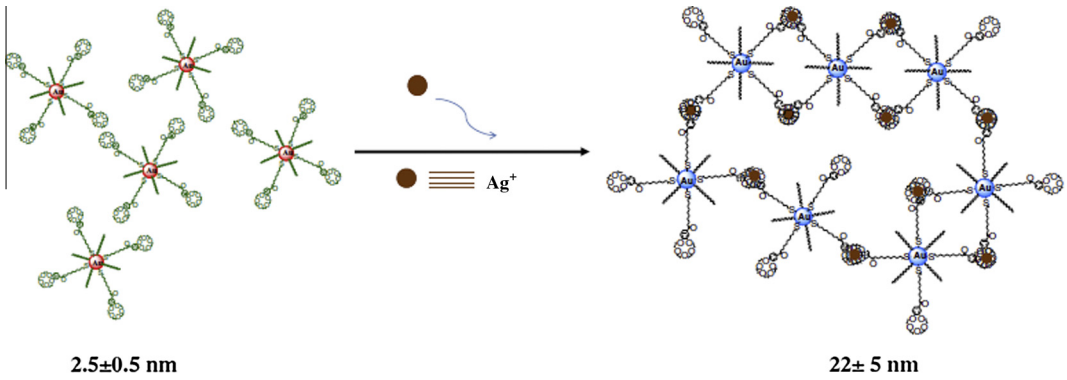
Scheme 14 A proposed mechanism of HSA binding onto surface of the Fe_3O_4-APTES-Crown (Bayrakcl et al., 2013).

It is well known that proteins covalently immobilized on the surface of magnetite nanoparticles based amino propyl group. This is via the chemical bonding between amine groups of silica and carboxy groups of proteins. HAS was also bounded on the surface of (Fe_3O_4-APTES-Crown) by non-covalent interaction between amine groups of protein and azacrown moieties of silica. A possible binding mechanism of protein to surface of magnetite nanoparticle containing azacrown moieties was proposed by the ionized amine group of the HSA, which was inserted in the crown moiety in a host–guest interaction (Scheme 14). This interaction between HAS and magnetite nanoparticle surface functionalized with azacrown moieties (Fe_3O_4-APTES-Crown ether) was compared with ungrafted magnetite nanoparticle (Fe_3O_4-APTES) and it was observed that the protein binding percentage of (Fe_3O_4-APTES-Crown ether) was higher than that of ungrafted derivative (Fe_3O_4-APTES). Based on these findings, it is expected that the robustness of immobilized capture protein on the surface of magnetite nanoparticle based azacrown ether by non-covalent interaction would be useful for protein–protein interaction studies which may require a series of washing steps in a solid phase system. Magnetite nanoparticles containing azacrown ether units can lead a rapidly easy separation and recovery from the reaction medium in an external magnetic field. By using an external magnetic field which is cheap, various applications can be designed in bioprocesses, biomedical devices and biomedicine, especially protein microarray systems.

Also a method for the modification of gold nanoparticles (Au-NPs) with benzo-15-crown-5 that led to the development



Scheme 15 Schematic illustration of synthesis and assembly of C4MPN-crown (Haghnazari et al., 2013).



Scheme 16 The possible mechanism for the aggregation of C4MPN-Crown in the presence of Ag^+ ion (Haghnazari et al., 2013).

of a colorimetric assay for Ag (I) ion has been reported (Haghnazari et al., 2013). The brown color of a solution of the modified Au-NPs turns to purple on the addition of Ag (I) ion. In this work an initial study of potentially novel sensing nanomaterials that utilize the ionophoric capacity of benzo-15-crown-5 was carried out. Interestingly, Ag^+ ion can be selectively recognized with this ionophore-AuNPs system even by the naked eye. The synthesis of butane thiol monolayer-protected nanoparticle modified with benzo-15-crown-5 planned is shown in Scheme 15.

These results indicated that common metal ions have no effect on the determination of Ag^+ ions and the current method is specific and selective for silver ion. This specificity could be attributed to the specific combination of C4MPN-Crown with Ag^+ ion in a 2:1 complexation as shown in Scheme 16.

The formation of this sandwich linking while benzo-15-crown-5 is incorporated onto the surface of gold nanoparticles may lead to a metal mediated nanoparticle aggregation, and therefore, colorimetric changes of the dispersions. To investigate this assumption and evaluate the data obtained from UV–visible studies, the morphology of the functionalized C4MPN crown before and after the addition of Ag^+ ions was studied by transmission electron microscopy. The averaged particle diameter for C4MPN-crown, deduced from the TEM, is 2.5 ± 0.5 nm and the image displays that the shape of these modified C4MPN crown is regular and close to spherical with a reasonable degree of monodispersity. The color detection limit of this method by naked eyes was 50 nM, and the lowest detection limit was approximately 12.5 nM. This simple and cost-effective sensing system demonstrates a great potential for the detection of heavy metal ions in real samples.

4. Conclusion

Although various methods for the determination of ions are available, many techniques often require quite expensive and time-consuming sample pretreatment, including preconcentration and matrix separation. Colorimetric sensors are cost effective and suitable for ions determination.

In particular, there are several advantages to using functionalized organic–inorganic hybrid nanomaterials as chemosensors in the environment. First, functionalized nanomaterials can rapidly and easily detect the metal ions. Second, these nanomaterials would be useful as efficient adsorbents for specific guest molecules in environmental pollutants. Third, the nanomaterials can be easily controlled to interact with target guest molecules for detection among various guest molecules in real analytical samples.

In these sensors the visual colors (or color changes) can be observed by naked eyes, and therefore no affiliated instruments are required. For example gold nanoparticles (AuNPs) are good materials for colorimetric sensors. Their extinction coefficients are significantly high.

A critical drawback of colorimetric methods based on nanoparticles is poor sensitivity; therefore, it would be desirable to design a colorimetric sensor to enhance the sensitivity of this detection. Recent studies have shown that the use of functionalized nanoparticles has been regarded as an effective strategy to enhance the sensitivity of colorimetric sensors. To recognize the target analyte, rationally tailoring the surface ligand of the NPs that can bind analyte is critical and essential. The ligand not only improves the stability of these nanoentities but also provides binding receptor for the target. Recently, crown ether molecule functionalized NPs for colorimetric tests have gained intense interest.

Since the colorimetric technique based on modified nanoparticles is a very simple, cost effective and sensitive, it is respected that in the future, colorimetric sensors based on nanoparticles will be developed with the various supramolecules for sensing many of cations, anions and also biological molecules. The mentioned advantages make it useful for rapid, convenient on-site detection and most likely possess great prospects in the future.

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Please cite this article in press as: Mohammadzadeh Kakhki, R., Rakhshanipour, M. Application of nanoparticle modified with crown ether in colorimetric determinations. Arabian Journal of Chemistry (2015), http://dx.doi.org/10.1016/j.arabjc.2015.07.012

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